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I here wish to express my personal thanks to Professor Remsen for the guidance he has given me in the present work, and my gratitude for the assistance and inspiration I have received from him during my whole stay at this University.

H. W. Hillyer

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Methods for Determining

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RELATIVE STABILITY

of the

Fatty Bromides.

THESIS OF HOMER W. HILLYER

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The subject of the strength of chemical affinity, or of the intensity of the force, to which chemical compounds owe their formation and their existence, is one which has of late, through the labors of various chemists, taken a prominent position in the chemical world. The idea of Mass-action, first advanced by Berthollet, though on false grounds, and since studied by so many chemists, has thrown much light on the general subject. This has been studied incidentally in connection with the researches on dissociation, and directly by Berthelot and Pean de St Gilles (1), Menschutkin (2), Ostwald(3) Gladstone and Tribe (4), Muir (5), Potilizin (6), and Hell and Urech ; and in a more theoretical way by Berthelot (1), Hurter (8), Harcourt and Esson (9), Guldberg and Waage (10), and Van't Hoff (11).

In some departments comparative studies have been made of the relative activity, or readiness to enter into reaction with a given reagent, of the members of a few series of compounds. Potilizin (6) experimented on the mutual displacement of Chlorine and Bromine, and Van't Hoff (12) and Menschutkin(13) experimented on the relative activity of the bases. In the field of organic chemistry, the fullest work has been done in

the study of comparative chemical activity by Berthelot, Menschutkin, and Ostwald. These studies have been almost entirely confined to determining the energy of reaction of the acids and alcohols. Of the alcohols by their reaction with a given acid (1, 2, 11) and of the acids in several ways ; viz., by their reaction with a given alcohol (1, 2, 11,), by the decomposition of their ammonium salts with formation of the amides (2), by their action on acetamide (3), by their power of inverting cane-sugar (3), and by the electric conductivity of their solutions (3). All of these are reactions in which the products of reaction tend to react in the opposite sense, thus bringing about, at the end of a certain period, a condition of equilibrium between the two reactions.

A few cases not involving acids have been studied. Of these, which are, in general, of the kind in which the reaction is not reversible, but few studies have been made. They will be mentioned in the sequel.

The desirability of research into the relative activity of the members of many classes of bodies may, perhaps, be best given by a quotation from Lothar Meyer's Modernen Theorien der Chemie :---

"It would be the problem of a science of comparative

affinity to set forth, in their dependence on the nature of the elements, the stability of chemical compounds, the changes to which they are subject or not subject, and to bring them under general rules. But, however great the number of observations made on the decomposition of chemical compounds may be, from a standpoint of comparison these have been considered and set forth in only limited measure. This has been done here and there for small groups of analogous and similar compounds, but in greater mearure only where it was of interest for the analysis or synthesis of compounds. Our treatises and text-books are almost entirely descriptive ; the study for a general science of comparative affinity, which bears to descriptive chemistry the same relation that comparative anatomy and physiology bear to systematic zoology, has not yet been made although it might rouse a more lively interest than the dry describing of substances". "What is here designated as stability of chemical compounds is in so far a relative conception, that it can be very different toward different agencies. Moreover it is the result not of one, but of very different causes, which are directed partially to the decomposition of the body and partially against it. But, before we can determine these single causes and separate their actions and the influence of each, it appears necessary to obtain as comprehensive views as possible

of the relations of the different classes of compounds, which rest as much as possible on quantitative measurements. By comparing analogous groups of compounds, establishing the differences and similarities, the material for a science of comparative affinity will be obtained, which will refer the relation of the compounds, the condition of their existence and decomposition to the properties of the atoms. The farther our knowledge advances in this direction, the more will chemistry lose the character of a preeminently descriptive science, to take up more and more that of a more strictly speculative one. Not as if there had not been speculation enough in chemistry (for there is indeed almost too much of that) but only in the sense that the speculation would get firmer and firmer foundations and be in condition to foresee with greater certainty than before the result of an experiment."

Some work having been done in this laboratory, last year by Mr. Keiser, on the relative stability of the bromides of some alcohol radicals, toward nascent hydrogen in alkaline solution, by treating their alcoholic solutions with sodium amalgam, it was proposed to me by Professor Remsen, to see whether the relative stability was the same toward nascent hydrogen in acid solution. The bromides experimented upon were those at hand; ethyl bromide, normal-and iso-propyl bromides, butyl bromide,

and amyl bromide b.p.119°. In view of the limited number of bromides, there was no expectation of doing much more at present than to search out methods, which could perhaps be more broadly used in the future. The scope of the research has changed somewhat during the progress of the work, so that the subject has now come to be the study of the relative stability of these bromides toward several reagents.

The first experiments which yielded any results were those in which the reducing agent was zinc with sulphuric acid. A solution containing 75 c.c. of equal parts of alcohol of about 94 per cent., and of sulphuric acid of about 10 percent., and an amount of bromide such that it contained 200 milligrams of bromine was placed in an Erlenmeyer flask of 125c.c. capacity. To this was added the zinc, which after ~~an action~~ an action of two hours and a half, was removed. The amount of reduction which had taken place was determined by estimating, by Volhard's method, the quantity of bromine abstracted. It was soon discovered that the nitrate of silver decomposed the bromides to a considerable extent, so that in the later experiments the method was to add the ferric sulphate and a small quantity of sulphocyanate solution and then titrate to disappearance of color, thus leaving the nitrate as short a time as possible in contact with the bromide. The titrating solutions

were so made that each cubic centimeter was equivalent to one milligram of bromine.

The reducing agent was of common sheet zinc cut in pieces of one inch by one half inch. These, after being bent in the middle at a right angle, so that they might, when resting on the two ends, expose as uniform an extent of surface as possible, were cleaned and slightly etched with dilute sulphuric acid, then washed, and placed in the flasks (four in each) by means of a platinum wire or small tapering glass rod bent at a right angle near the end.

In this way ethyl bromide, iso-propyl bromide, and butyl bromide were examined; but it was found that a larger per centage of alcohol was necessary for the solution of the amyl bromide, so that in a second series, in which iso-propyl, amyl, and normal propyl bromides were examined, the solvent was of 50 c.c. alcohol and 40 c.c. acid. The figures indicate the total number of milligrams of bromine abstracted from the organic bromides. This will be adhered to throughout the paper. All of the experiments of shorter duration described in this paper were carried on in flasks surrounded by flowing water of some nine or ten degrees of temperature. The flasks in the other experiments were also put in water to prevent any rapid initial activity, but the flow of water was not kept up, thus allowing the temperature to vary with that of the laboratory.

Series I.

Experiment I.	Butyl	3.9	Ethyl	not measurable.	
" II.	"	3.9	"	.7(?)	
" III.	"	3.9	"	.6 and	1.2
" IV.	"	3.3	Isopropyl	10.6 "	8.4
" V.	"	3.3	"	9.6 "	7.8

Series II.

Experiment I.	Isopropyl	6.7	Amyl	3.2 and	3.2
" II.	"	5.87	N. propyl	.7 "	.7

Though the results were very faulty, they were of great interest ; as their tendency was in a direction directly opposite to that obtained by Mr. Keiser in his experiments in alkaline solution. His results showed that ethyl and propyl bromides were most acted on, in alcoholic solution, while amyl bromide was very little acted on ; but, from the above experiments, it seems that ethyl and propyl are very stable toward nascent hydrogen in acid solution, while on amyl and butyl the effect is greater. In both acid and alkaline solutions however, the isopropyl was acted on more than the normal.

The difficulties lying in the way of such an investigation are ; that, with an alcohol sufficiently strong to hold the bromide in solution, the sulphate of zinc formed by the reaction soon crystallizes out, making the action irregular or

almost entirely stopping it, by depositing on the zincs. This renders a long continued action impossible, if the action is at all rapid. If the acid is more dilute, the formation of sulphate is slow, but in the same degree the evolution of hydrogen is also slow.

In a second series of experiments, 44 c.c. alcohol, 14 c.c. water, 2 c.c. sulphuric acid, and the same quantities of bromides as before were acted on. The action was slow, but, after it had continued over night, there was found crystallized out, in some of the flasks, a considerable quantity of zinc sulphate. To each flask was then added 16 c.c. water and 4c.c. sulphuric acid to dissolve the zinc sulphate and put the system again in action. After twenty-four hours farther action, there was a farther deposition of zinc sulphate, which was dissolved by addition of 20 c.c. water. The zincs were then removed and the reduction measured by drawing off from each flask 20 c.c. and titrating. The series was made up, in this case, of four portions of each bromide experimented on, one of which was not treated with zinc at all, the other three were treated with four of the zinc strips spoken of above. The portions with no zincs were intended to serve as controls, by which to determine whether the decomposition was due to the nascent hydrogen or to the other substances present ; and also,

in case of there being any previous decomposition of the bromides, to indicate to what extent it had taken place ; so that by substraction the action of the nascent hydrogen could be determined. As might be expected, with so many complications due to the deposition of sulphate of zinc and to the subsequent additions of water, the results are not very concordant among themselves and are not entirely confirmatory of the order of stability as given by the last series. The tendency, as it has been stated above, still holds ; that is, ethyl and propyl bromides are more stable than the other three.

	Zn.	No Zn.	Difference.
Ethyl	.3		
"	.35		
"	.45	.0	.35
Propyl	.4		
"	.5	.0	.45
Isopropyl	2.7		
"	2.5		
"	3.0	.35	2.37
Butyl	.9		
"	.95	.35	.57
Amyl	2.4		
"	2.35		
"	2.45	.4	2.0

The order of stability indicated , ethyl .35 propyl .45 butyl .57 amyl 2.0 isopropyl 2.4

As these indications were so clearly in disagreement with those obtained when the reduction was brought about by sodium, it was thought desirable to determine whether nascent hydrogen acted on the bromides in the same way, in alkaline solution, when it was produced in some other manner.

It had been observed that when zinc is put into an ammoniacal solution of cobalt sulphate , it soon becomes coated with a firm, glossy coating of cobalt, and that it is then a much more active reducing agent than before. Starting from this idea, it was found that quite a good evolution of hydrogen could be obtained in alcoholic soda with strips of zinc like those described above, after they had been coated with cobalt. The strips were bent, cleaned with sulphuric acid, and washed. All those to be used in a comparative experiment were treated alike, being placed in a shallow dish resting on their ends, and flooded with a strongly ammoniacal solution of cobalt sulphate containing one or two grams to the liter, and sufficient ammonium sulphate to keep the cobalt in solution as double sulphate. The zincs were allowed to remain in this for a short time till there was quite a rapid evolution of hydrogen, when the solution was poured off and the zincs washed.

They were, in general, rendered more active by treatment with very dilute sulphuric acid and washed a second time with several changes of water ; though it was not possible to remove the acid so completely that they would not free some hydrogen when placed in distilled water.

In the first experiments, a large number of zincs were treated at once with the cobalt solution, with the idea of making them of equal reducing power. The caustic soda solution was made from sodium by dissolving about sixty-five grams of sodium in a liter of alcohol of about 75 per cent.

The solutions, when in action, contain 30 c.c. alcohol, 20 c.c. water, 10 c.c. soda solution, and a quantity of bromide containing 200 milligrams of bromine. The soda was added by means of a pipette, as rapidly as possible to the different flasks making up a series for comparison. At the end of the action, the zincs were removed in the order in which they had been introduced ; thus securing a very nearly equal period of time for the action of the zincs in each flask. An equal quantity of nitric acid was then added to each flask sufficient to neutralize the alkali, so that there were, for the action of the alkali, very nearly equal periods of time . In order to have a control of the rate of action, in each case there was one flask with ethyl bromide and no zincs and one with ethyl

bromide and four zincs. Parallel with these, was run a series containing eight other flasks with some other bromide, four with four zincs and four with no zincs, with the idea of finding the action due to the hydrogen, by substracting from the total the amount of decomposition which had taken place, when there were no zincs. The systems were in action over night, or about sixteen hours.

First Day's Experiment.

	Zn.	No Zn.	Difference.
Ethyl	46.2	28.7	17.5
Amyl	17.8	4.9	
"	19.9	4.2	
"	19.2	4.5	
"	19.9	4.9	
Mean	19.2	4.6	14.6

Second Day's Experiment.

	Zn.	No Zn.	Diff.
Ethyl	44.1	26.6	17.5
Butyl	12.4	3.4	
"	12.4	3.1	
"	11.9	3.4	
"	12.9	3.4	
Mean	12.4	3.3	9.1

Third Day's Experiment.

	Zn.	No Zn.	Diff.
Ethyl	42.0	26.4	15.6
Isopropyl	13.7	3.5	
"	13.5	3.3	
"	14.0		
"	13.7		
Mean	13.7	3.4	10.3

For some cause, the action was less on the ethyl bromide used as a control in the third day's experiment, and it was thought thatthere would probably be less, in case of the other bromides also. So it was thought best to run a full series of the bromides simultaneously, that they might be as much as possible under the same conditions. Three such series were made, but now they are not comparable with one another, as the temperature might not be exactly the same, and the reducing-power of the zincs would be different, being made fresh each time. The members of the series are, however, now comparable.

Series,	I.	II.	III.	
Ethyl	40.9	54.2	20.6	Zn.
"	28.0	35.7	19.6	No Zn.
"	12.9	18.5	1.0	Diff.
N. Propyl	24.5	32.2	9.4	Zn.
"	9.8	11.9	7.3	No Zn.
"	14.7	20.3	2.1	Diff.
Isopropyl	11.5	16.4	9.1	Zn.
"	5.6	4.9	3.1	No Zn.
"	5.9	11.5	6.0	Diff.
Butyl	11.2	12.6	4.2	Zn.
"	3.5	3.8	3.3	No Zn.
"	7.7	8.8	.9	Diff.
Amyl	16.8	18.5	6.3	Zn.
"	4.5	5.6	4.2	No Zn.
"	12.3	12.9	2.1	Diff.

These results, so little concordant, can only be used, as were those in the acid series, to show general tendencies. Whether with or without zincs, the ethyl and normal propyl

bromides are decomposed more readily than the other three.

As isopropyl bromide is more readily decomposed by action of zinc and sulphuric acid than the normal bromide, while the opposite is true in alkaline solution, it was thought best to study these in their action toward different reagents and to return to the study of the other bromides later. Standard solutions were made by dissolving 3.8437 grams of each bromide in 250 c.c. alcohol. Each cubic centimeter would then contain 10 milligrams of bromine. The substances were weighed in tubes of about 8 by 180 m.m. drawn to a point. One of these, after making a file scratch near the point, was placed on the balance pan in an upright position in a small beaker. After weighing, 3.8437 grams were added to the other pan and enough of the bromide was run in, by means of a narrow glass tube drawn to a point, and used as a pipette to again bring to a balance. It was not difficult, after a little practice, to weigh in this manner to within a milligram. The point of the weighing tube, being thrust into the mouth of a 250 c.c. measuring flask, was broken off by pressing it against the inside of the neck of the flask. The bromide having run into the flask, the tube was immediately rinsed out by pouring alcohol through it. The flask having been filled to the mark with alcohol, the contents were, after thorough mixing, transferred to tightly stoppered

bottles.

To 20 c.c. of each of these solutions was added 20 c.c. of aqueous ammonia of 10 per cent. At the end of about 20 hours the bromine freed was, in case of the normal bromide 25.4 mgr. in one flask, 29.2 mgr in another ; in case of the iso-bromide it was 3.8 mgr., 4.2 mgr. and 5.0 mgr. in different flasks, thus showing that the action of ammonia is of the same order as that of soda.

Three flasks were prepared, containing 20 c.c. normal propyl bromid solution, 10 c.c. alcohol and 10 c.c. soda solution. Into two of these were put two pieces of aluminium foil, having the same size and shape as the zinc strips used above. A similar set of flasks was prepared with the iso-bromide. After the action had continued five hours, the aluminium was removed, the solutions neutralized with nitric acid and titrated, with the following results :

	With Al.	No Al.	Diff.
Normal,	9.2		
Normal,	10.0	8.8	.8
Iso	7.4		
,,	7.2	4.8	2.5

From which it appears that though the normal bromide is most affected, both with and without the aluminium, the difference between the two actions, or the action of the nascent hydrogen,

is much greater in case of the iso bromide. This, taken in connection with the indications of the experiment with zinc in acid solutions, makes it probable, that, as far as the action of nascent hydrogen is concerned, the normal bromide is more stable.

20 c.c. normal propyl bromide solution,

5 c.c. dilute nitric acid, and

25 c.c. silver nitrate solution, containing silver equivalent to 25 mgr. bromine, were set for 16 hours in a dimly lighted place. At the end of that time, there was considerable opalescence, and some deposition of silver bromide. By titration, it was found that 2.7 mgr. of bromine had combined with silver. A similar mixture containing the secondary bromide was found to have deposited a heavy yellowish-white precipitate of silver bromide ; on titration, it was found that, of the 25.0 mgrs. of bromine, with which the silver added was capable of combining, 24.3 mgrs. were thus combined. From a mixture containing 20 c.c. bromide solution, and 20 c.c. of a neutral solution of silver acetate, capable of precipitating 20.2 mgr. bromine, 19.2 and 19.2 mgr. bromine were found precipitated in two parallel experiments, by the iso bromide, while only 2.5 mgr. and 2.5 were precipitated by the normal bromide.

Mixtures were made, containing 20 c.c. bromide solution, and 10 c.c. acetic acid of ordinary strength. These were allowed to act for two hours, twenty minutes on six cobalt zincs prepared as above. The bromine freed was, in case of the normal bromide, 2.0 and 1.9 mgrs. in different flasks ; in case of the iso-bromide 8.0 and 8.1 mgrs. By adding sufficient nitric acid, all of the red ferric acetate, formed by adding the ferric sulphate, may be changed to the colorless nitrate, so that the titration by Volhard's method presents no difficulties. The action of this mixture of alcohol and acetic acid on the cobalt zincs, gives a very regular evolution of hydrogen, which, though not very rapid, may be continued for five or six hours before the zinc acetate begins to crystallize out, thus giving time for a considerable reduction.

The form of zinc was now changed to that of a flat spiral made by winding a strip of zinc one half inch by 24 inches about a small core, then unwinding and loosening the coil till no two turns came in contact. The coil was placed in a beaker, which contained the solution of the bromide to be reduced, and a small glass rod, so bent as to make a support for the coil, thus ensuring free circulation.

Through some fault in the coating of the zincs, the reduction was, in the first experiment, not greater than in the

last case. With 40 c.c. bromide solution, 20 c.c. acetic acid, and 20 c.c. alcohol, the normal bromide yielded to the action, in each of the parallels, 1.8 mgrs. bromine, the iso bromide 7.2 mgrs. bromine, in one case, and 6.6 mgrs. bromine in the other.

In a second set of parallels in which the conditions were the same, except that the zincs were better and the action for about five hours, the normal bromide yielded 4.5 and 4.8, the iso bromide yielded 20.0, and 20.1 mgrs. bromine.

The reductions, though small, were still so large, that it was thought desirable to make an experiment on all of the five bromides. For this purpose, standard solutions were made of the same molecular concentration as with the propyl bromides. The conditions were the same as regards amount of bromide, of alcohol, and of acid as in the last case. The zincs were, however, different. At the end of five hours action titration gave the following results :

Ethyl	1.2	and	1.5
I. propyl	10.5	,,	11.7
N. propyl	3.3	,,	3.3
Butyl	6.0	,,	6.0
Amyl	9.9	,,	9.9

It was afterwards found that the amyl and butyl bromide solutions gave some indications of bromine already abstracted

by standing in alcoholic solution. This may change their apparent stability somewhat, though the evidence of the next experiment is to preserve the order given.

2 c.c. bromide solution, 20 c.c. standard silver nitrate solution, 20 c.c. alcohol, 2 c.c. nitric acid were allowed to act on one another for 67 hours, with the view of determining whether all of the bromine would be abstracted from the organic bromides when there was excess of silver. With this concentration, however, the action was too small to titrate conveniently ; but the indications given by the opalescence showed that the action was least with the ethyl bromide and greater with the others, in the following order ; normal propyl, butyl, amyl, and iso propyl.

As was stated at the beginning of this paper, the object of the work at the present time was to search out methods to see which gave promise of results, that they might be more exactly worked out in the future. It seems that the reduction with zinc and acids is not capable of yielding results which are very reliable. The actions of zinc and of aluminium in alkaline solution are so complicated by the independent action of the alkali alone, that they are of little value. In the same way, the action of sodium amalgam is also complicated by the increasing alkalinity of the solution.

The most promising fields of research are those with the salts of silver in concentrated solution of the bromides, and the action of ammonia and of soda alone. That the last is one which would be good for study may be seen from the following experiment :

20 c.c. bromide solution, 10 c.c. alcohol, and 20 c.c. soda solution were placed in each flask. The solutions of bromides were the same as those used in the last experiment with cobalt zincs and acetic acid. The soda was made by action of water on sodium amalgam, and contained about 10 per cent sodium-hydroxide.

Of the two hundred milligrams of bromine in each flask, the following amounts were abstracted :

Ethyl	165.6	or	82.8 per cent.
,,	159.2	,,	79.6 ,,
N. propyl	130.5	,,	65.2 ,,
I. propyl	50.4	,,	25.2 ,,
Butyl	31.2	,,	15.6 ,,
,,	32.2	,,	16.1 ,,
Amyl	65.8	,,	32.9 ,,
,,	67.6	,,	33.8 ,,

The re-action was, in all probability this $C_nH_{2n+1}Br + C_2H_5OH + KOH = C_nH_{2n+1}OC_2H_5 + KBr. + H_2O$ that is the forma-

tion of the mixed ether of ethyl, and of the radical of the bromides used. In the above experiments the odor of common ether was very strong in the flask with ethyl bromide. In the flask with propyl bromide, there was also a very pleasant odor, very like that of common ether, and quite different from the odor of the bromide solution. An experiment, in which a larger but unknown amount of normal propyl bromide was treated with alcohol and caustic soda, was performed. After standing a week or two, the mixture was made very nearly neutral with nitric acid, and subjected to distillation, when a small quantity of a volatile liquid was obtained, which had an odor very much like that of common ether, and a density less than that of water. The quantity was too small to determine its boiling point. There are several cases known (14) in which mixed ethers have been made by treating halogen derivatives of the hydrocarbons with alcoholic potassa at an elevated temperature, but it is thought that this is the first time that such a reaction has been noted at common temperatures.

Reactions which are slow, but complete, have been studied in several cases. Wislicenus (15), by acting on various haloid ethers with the sodium compounds of aceto-acetic ether, ethyl aceto-acetic ether and malonic ether, without external application of heat, found the order of stability of some com-

pounds which must be considered in connection with the above list. In order of increasing stability, Wislicenus finds methyl iodide, ethyl iodide, primary propyl iodide, ethyl bromide, primary isobutyl iodide, primary propyl bromide, tertisry butyl bromide. Or, taking the iodides alone methyl, ethyl, primary propyl, secondary propyl, isobutyl, which is the same order as that obtained, by the action of alcohol and soda, in the last experiment. The ethyl bromide is less stable than the primary propyl bromide and that, than the tertiary butyl bromide.

In 1881 Prof. C. L. Jackson of Harvard (16), studied the relative stability of certain substituted benzyl bromides. By action of a solution of sodium acetate in alcohol on the ortho-, meta-, and para brombenzyl bromides at 100 degrees, he found that the ortho bromide was most stable toward this reagent, the meta next, and the para least stable.

For a single compound, the study of a reaction which is slow, but complete, has been made by Buchanan (17) and by Van't Hoff and Schwab (18), of the decomposition of chloracetate of soda by sodium hydroxide. But, on this kind of reaction, which slowly completes itself, no studies, except those mentioned above, have been made with a view of comparing the relative stability of the members of a class of compounds.

It should be the object of future study to determine the relative stability of these and other bromides toward alcoholic soda and toward ammonia, and also to study the stability of corresponding compounds of chlorine and iodine. According to Prof. Jackson para-chlor, para-brom and para-iodo-benzyl bromide are equally stable ; while, according to the results of Wislicenus, the iodides are less stable than the corresponding bromides, and these, than the corresponding chlorides in the fatty compounds experimented on. It will be of great interest to determine whether this will hold in these reactions also.

Studies should also determine the action of silver salts on these bromides, and on the other halogen compounds ; for, though not so well adapted to finding the true relative stability, it will be of great interest to determine, if possible, what law governs the order of the stability of compounds having the same constitution, but containing different halogens; and of those having different molecular weights in one case and different constitutions in the other, but containing the same halogen.

Before it can be determined whether there is a different ratio of stability between the members of such a class of compounds when acting with a given reagent, it would be necessary to make a study of the reaction quantitatively from its begin-

ning to its completion, and not to take, as has here been taken, the ratio of decomposition after a definite long period of time. With those compounds which enter into the reaction most readily, the conditions change most rapidly. In this case, the concentration and strength of alkali change most rapidly with ethyl bromide; so that, at the end of a certain time, it is under conditions less favorable for the reaction, than the others, whose action has been slower. When, however, the whole series has been studied under like conditions of temperature from the commencement of reaction till the limit is reached, by comparing the rapidity of action of the several members, at the times at which the reaction has gone on to the same extent with each, we would have, at every such point, a measure of the relative stability of the several members ; since they are, at these points, under like conditions of dilution. This may be graphically represented by a series of hypothetical curves, in which the abscissas represent time,the ordinates, percentages of decomposition. Chemical activity would be represented by the inclination of the curves at the points in which a horizontal line indicating that a certain amount of bromide had been acted on in each case, cut the curves. In such a series of curves, the data of the experiments with the alcoholic soda would be represented by the vertical distances from the axis of abscis-

sas to the points in which the curves cut a vertical line erected at the point which indicates a time of five days. The most stable bromides are relatively even more stable than they appear by the data given.

The facts derived from these experiments tend to show that the primary bromides of lower molecular weight are more easily acted upon, by alkaline reagents, than those of higher molecular weight ; while they are less acted on by acid reagents ; with the second class, must also be put secondary propyl bromide.

Before a general conception can be formed of what is meant by saying that one body is more stable than another, all the scattered facts, relating to the formation and decomposition of those bodies in various ways, must be brought together and harmonized. A few such facts, which have been collected, especially in regard to the propyl compounds, will be here considered:

1). When normal propyl bromide is heated with aluminium bromide, it is changed to isopropyl bromide (19), probably, as explained by Wöhler, by breaking up into propylene and hydrobromic acid; which, when present together, are known to unite with formation of isopropyl bromide. 2). Normal propyl amine, when treated with nitrous acid, is changed to isopropyl alcohol (20).

3). Isopropyl bromide, when acted on by alcoholic soda, is more stable than the normal bromide. 4). Isopropyl iodide, when acted on by the sodium compound of aceto-acetic ether etc., is more stable than the normal. 5). Isopropyl alcohol is less easily made into compound ethers than the normal.(21). 6). Propane, when treated with bromine, yields normal propyl bromide. 7). When propyl-isopropyl bromide is treated with hydriodic acid at low temperatures, isopropyl iodide and propyl alcohol are formed.(22).

8). When isopropyl bromide is treated with silver acetate or nitrate, it is more easily decomposed than the normal bromide. 9). When isopropyl bromide is acted on by zinc and an acid, it is more easily acted on than the normal bromide. This is probably the action of nascent hydrogen in alkaline solution also.

These facts do not yet fall under any general statement. In the first and second of the above paragraphs, the facts tend to show, that a body in the secondary position in propane, is held more strongly than in the primary. In the third paragraph, the opposite is the case.

For the present we leave the subject in this state, adding a bibliography of the articles referred to.

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